

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOSHIBA CORP

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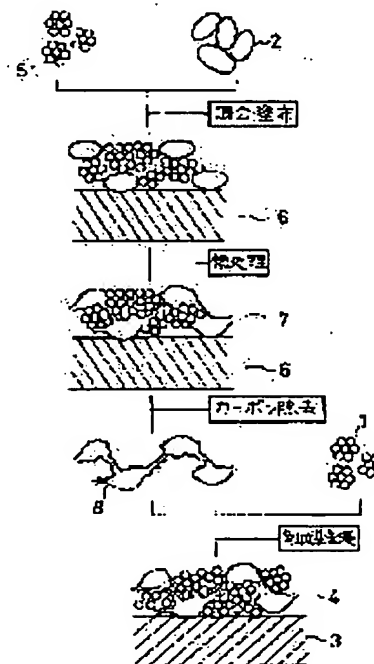
(72)Inventor : NAGAMORI YASUHIKO

(54) MANUFACTURE OF ELECTRODE CATALYST LAYER FOR PHOSPHORIC ACID TYPE FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method of an electrode catalyst layer for a phosphoric acid type fuel cell in which battery characteristics are enhanced by preventing the reduction of the available surface area of platinum or platinum alloy resulting from the coating of fluororesin without damaging the water repellency of a catalyst layer.

SOLUTION: In a manufacturing method of an electrode catalyst layer for a phosphoric acid type fuel cell made of a mixture of a catalyst which is composed of platinum or platinum alloy and carbon supporting the same, and fluororesin, the mixture of carbon 4 and the fluororesin 2 is uniformly applied onto support material 6, is heat-treated so as to form a layer 7. Thereafter, the catalyst 1 is impregnated into a fluororesin sheet 8 in which a fine fluororesin network is produced by removing the carbon only. Thereby, since the dissolving of the fluororesin 2 and the mixing with the catalyst 1 are conducted in separate processes, the occurrence of a coating onto the surface of the platinum or the platinum alloy by the dissolved fluororesin is not allowed so that the reduction of the available surface area of the platinum or the platinum alloy in the catalyst layer can be prevented.



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CLAIMS

[Claim(s)]

[Claim 1] In the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells which serves as a catalyst which consists of platinum or a platinum alloy, and carbon that supports this from mixture with fluororesin After applying and heat-treating the mixture of carbon and fluororesin to homogeneity on supporting material and forming a layer, The manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells characterized by sinking a catalyst into the fluororesin sheet with which the network of the detailed fluororesin generated by removing only carbon was formed.

[Claim 2] The manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells characterized by removing by impressing potential to this layer and electrolyzing carbon after applying and heat-treating the mixture of carbon and fluororesin to homogeneity on supporting material in the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells according to claim 1 and forming a layer.

[Claim 3] The manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells characterized by using gold or platinum as a supporting material in the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells, and relates to the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells which prevented reduction of the available surface area of the platinum in a catalyst bed, or a platinum alloy especially.

[0002]

[Description of the Prior Art] The phosphoric acid fuel cell is known as equipment which changes into direct electrical energy the chemical energy which the fuel has from the former. This phosphoric acid fuel cell is what took out electrical energy from between two electrodes using the electrochemical reaction which occurs by supplying fuel gas, such as hydrogen, to one electrode, and supplying oxidant gas, such as oxygen, to the electrode of another side, and as long as fuel gas and oxidant gas are supplied, it can usually take out electrical energy at high effectiveness, while it arranges the electrode of a pair on both sides of a phosphoric-acid electrolyte.

[0003] Usually, the electrode of this kind of phosphoric acid fuel cell consists of a catalyst bed for promoting electrochemical reaction, and a carbon plate which supports this catalyst bed. The catalyst bed is constituted by the catalyst which consists of platinum or a platinum alloy, and carbon that supports this, and fluororesin, and is usually manufactured as follows.

[0004] That is, as shown in drawing 4, a catalyst 1 and fluororesin 2 are mixed first. Next, after applying this mixture to homogeneity and sticking it by pressure with a roller on the carbon plate 3, finally a catalyst bed 4 is formed by heat-treating this sticking-by-pressure object in predetermined temperature and time amount in a furnace. Next, the electrode with which the network of detailed fluororesin 2 was formed in the catalyst bed 4 interior is manufactured by dissolving fluororesin 2 by heat treatment. Thus, by the water repellence of fluororesin 2, in the catalyst bed 4, the manufactured electrode secures the space where it does not sink into a phosphoric-acid electrolyte, and is utilized as passage of a fuel/oxidant gas while it raises the binding property of the catalyst bed 4 interior. Moreover, if the amount of mixing of fluororesin 2 is changed, the amount of sinking in of the phosphoric-acid electrolyte in a catalyst bed 4 can be adjusted.

[0005] Generally, the water repellence of a catalyst bed is gradually lost by degradation of fluororesin, oxidation of carbon, etc. under the service condition of a fuel cell. For this reason, when the pore which is the passage of a fuel/oxidant gas is blockaded with a phosphoric-acid electrolyte with operation of a fuel cell, the diffusibility of a fuel/oxidant gas will fall and a cell property will also fall. In order to control the fall of the cell property of such a fuel cell with time, the amount of mixing of fluororesin is increased to some extent, and it is necessary to raise the water repellence of a catalyst bed.

[0006]

[Problem(s) to be Solved by the Invention] However, if the amount of fluororesin mixing of a catalyst bed is increased in order to raise the water repellence of a catalyst bed, in case fluororesin will be dissolved by heat treatment, the front face of the platinum with which electrochemical reaction is actually performed, or a platinum alloy will be covered with dissolved fluororesin, and the problem that available surface area decreases arises.

[0007] The platinum of carbon support is used for a catalyst here, and the example which

investigated the relation between the amount of fluororesin mixing and the rate of the platinum surface area actually used for electrochemical reaction by half cell trial is shown in drawing 3.

[0008] In this drawing, when the amount of mixing of fluororesin is 35wt(s)%, about 93% of the supported platinum surface area is used for electrochemical reaction, but if available platinum surface area decreases and becomes amount of mixing 50wt%, it will decrease to about 75%, as the amount of fluororesin mixing increases. That available platinum surface area decreases means that the cell property is falling.

[0009] If the amount of fluororesin mixing of a catalyst bed is increased, although the rate to which a phosphoric-acid electrolyte sinks into a catalyst bed will become slow and a battery life will become long, on the other hand, the surface area of the platinum contributed to electrochemical reaction or a platinum alloy will decrease, and a cell property will fall.

[0010] This invention was made in view of the above-mentioned situation, and the purpose is in offering the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells which prevented reduction of the surface area of the available platinum by covering of fluororesin, or a platinum alloy, and aimed at improvement in a cell property, without spoiling the water repellence of a catalyst bed.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, claim 1 of this invention In the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells which serves as a catalyst which consists of platinum or a platinum alloy, and carbon that supports this from mixture with fluororesin After applying and heat-treating the mixture of carbon and fluororesin to homogeneity on supporting material and forming a layer, it is characterized by sinking a catalyst into the fluororesin sheet with which the network of the detailed fluororesin generated by removing only carbon was formed.

[0012] In the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells according to claim 1, after claim 2 of this invention applies and heat-treats the mixture of carbon and fluororesin to homogeneity on supporting material and forms a layer, it is characterized by removing by impressing potential to this layer and electrolyzing carbon. Claim 3 of this invention is characterized by using gold or platinum as a supporting material in the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells according to claim 2.

[0013]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to drawing. Drawing 1 is the schematic diagram showing the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells which is one example of this invention.

[0014] In this drawing, fluororesin 2 used TFE (tetrafluoroethylene) powder and supporting material 6 used a golden mesh for that to which the catalyst 1 supported platinum with the 20wt(s)% rate to carbon, respectively.

[0015] First, 10:8 carried out fluororesin 2 and carbon 5 comparatively, it agitated and mixed in the solvent containing a dispersant, and paste-like mixture was obtained. It is this paste-like mixture 10x10cm 2 It applied to supporting material 6 by the screen printer at homogeneity. Heat treatment was performed for about 10 minutes in the furnace maintained at 340-degree C nitrogen-gas-atmosphere mind in this, and the layer 7 was formed in supporting material 6. Thereby into a layer 7, the network of detailed fluororesin is formed.

[0016] Next, this layer 7+ supporting material 6 is dipped into 1M sulfuric acid, the potential of 1.2V is applied, only the carbon 5 in a layer 7 is removed by electrolytic etching, and the fluororesin sheet 8 formed in the network of detailed fluororesin is obtained. And the fluororesin sheet 8 is stuck by pressure with a roller on the carbon plate 3, and it carries out suction sinking in of the catalyst 1 from the fluororesin sheet 8 side, decompressing the carbon plate 3 side, and a catalyst bed 4 is formed on the carbon plate 3. Under the present circumstances, it is not heat-treating to a catalyst bed 4. Moreover, he is trying to set the weight ratio of the catalyst 1 at this time, and the fluororesin sheet 8 to 1:1. That is, the amount of fluororesin mixing is 50wt(s)%.

[0017] Thus, as a result of measuring the utilization factor on the front face of platinum in the produced catalyst bed 4 by half cell trial, the utilization factor on the front face of platinum was 95% or more. As mentioned above, by performing at another process formation of a detailed fluororesin

network and sinking [of a catalyst 1] in in, covering to the catalyst by the fluororesin 2 which dissolved by heat treatment, i.e., a platinum front face, did not occur, but reduction of platinum surface utilization percentage was able to be prevented. [which it has already heat-treated] [0018] Furthermore, the operation hysteresis of the cell using the electrode which formed this catalyst bed 4, and the operation hysteresis of the cell using an electrode with the catalyst bed by the conventional approach were shown in drawing 2 . In drawing 2 , in the catalyst bed by the conventional method, if the amount of fluororesin mixing is increased from 40wt(s)% of case (characteristic curve 9) to 50wt(s)% (characteristic curve 10), although the life of a cell is extended, the cell voltage in early stages of a generation of electrical energy will fall. On the other hand, in the case of the catalyst bed (characteristic curve 11) by this invention, in spite of making the amount of fluororesin mixing into 50wt(s)%, even if it compares with the case (characteristic curve 9) where the utilization factor on the front face of platinum is 40wt(s)% of the conventional example, since it is high, the early stages of a generation of electrical energy to the electrical potential difference is longer [a battery life] than the case (characteristic curve 10) of 50wt(s)% of the conventional example highly.

[0019]

[Effect of the Invention] Since the dissolution of fluororesin and mixing with a catalyst are performed at a separate process according to the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells of claim 1 of this invention as explained above, covering to the platinum by dissolved fluororesin or a platinum alloy front face does not occur, but reduction of the available surface area of the platinum in a catalyst bed or a platinum alloy can be prevented.

[0020] According to claim 2 of this invention, it becomes possible by removing carbon electrochemically rather than removing carbon physically and mechanically to remove completely the carbon caught by the detailed fluororesin network.

[0021] Since it becomes possible to perform electrolysis processing as it is by there being conductivity and forming the layer of the mixture of carbon and fluororesin on the mesh of stable gold or platinum chemically according to claim 3 of this invention, it can work more easily.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram showing the manufacture approach of the electrode catalyst bed for phosphoric acid fuel cells of one example of this invention.

[Drawing 2] Drawing having shown the property of the fuel cell using an electrode with the conventional catalyst bed, and an electrode with the catalyst bed by this invention with the passage of time.

[Drawing 3] Drawing showing the amount of fluororesin mixing of the electrode catalyst bed for phosphoric acid fuel cells and the utilization factor on the front face of platinum of a catalyst bed by the conventional manufacture approach.

[Drawing 4] The schematic diagram showing the manufacture approach of the conventional electrode catalyst bed for phosphoric acid fuel cells.

[Description of Notations]

1 [-- A catalyst bed, 5 / -- Carbon, 6 / -- Supporting material, 7 / -- A layer, 8 / -- Fluororesin sheet.]
-- A catalyst, 2 -- Fluororesin, 3 -- A carbon plate, 4

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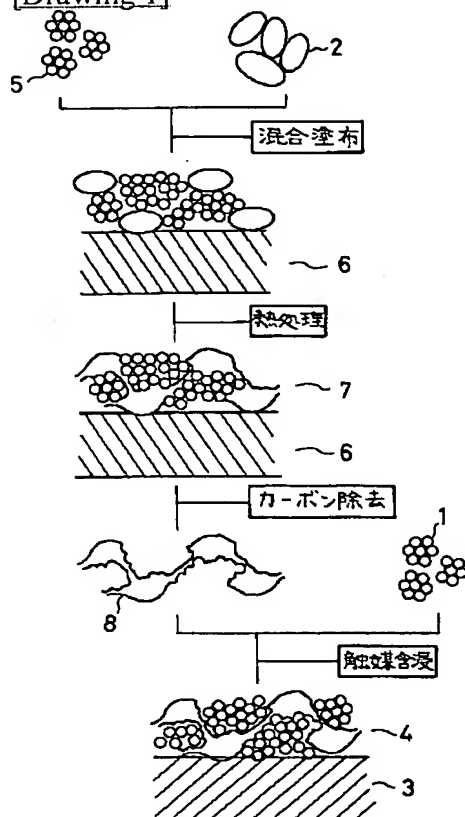
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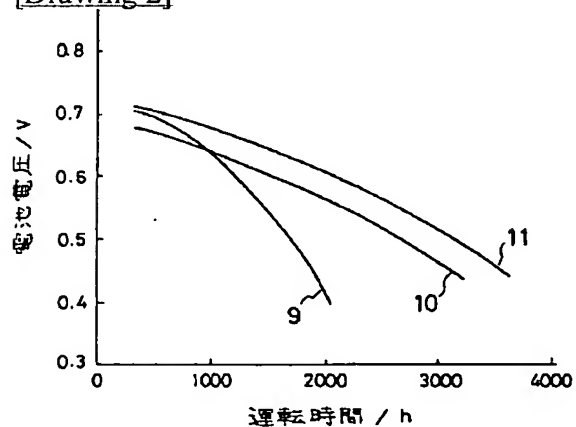
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DRAWINGS

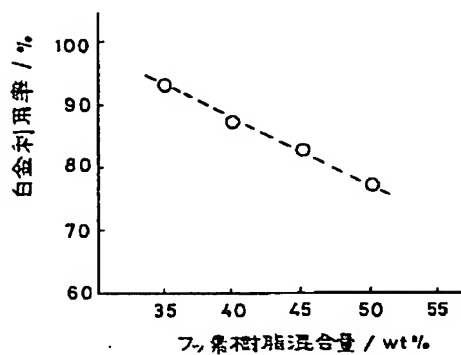
[Drawing 1]



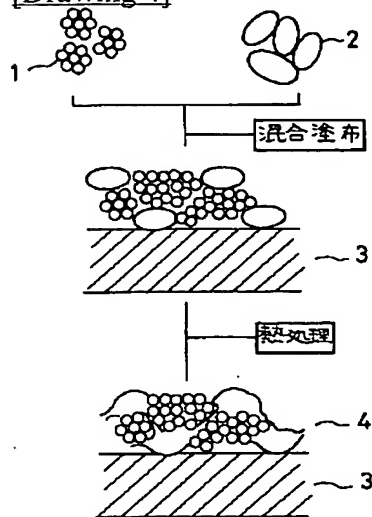
[Drawing 2]



[Drawing 3]



[Drawing 4]



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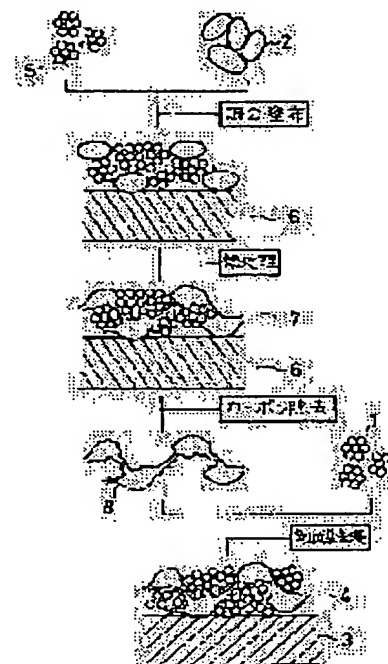
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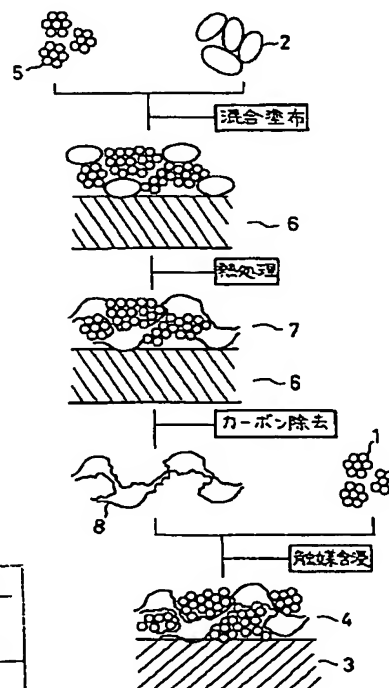
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(54) 【発明の名称】 リン酸型燃料電池用電極触媒層の製造方法

(57) 【要約】

【課題】触媒層の撥水性を損うことなく、弗素樹脂の被覆による利用可能な白金、あるいは白金合金の表面積の減少を防止して電池特性を向上を図ったリン酸型燃料電池用電極触媒層の製造方法を提供すること。

【解決手段】白金、あるいは白金合金とこれを担持するカーボンとからなる触媒と、弗素樹脂との混合物からなるリン酸型燃料電池用電極触媒層の製造方法において、カーボンと弗素樹脂との混合物を支持材上に均一に塗布し、加熱処理して層を形成した後、カーボンのみを除去することにより生成された微細な弗素樹脂のネットワークが形成された弗素樹脂シートに触媒を含浸しているので、弗素樹脂の溶解と、触媒との混合が別々の工程で行われるため、溶解した弗素樹脂による白金、あるいは白金合金表面への被覆が発生せず、触媒層中の白金、あるいは白金合金の利用可能な表面積の減少を防止することができる。



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SEARCH REPORT

【特許請求の範囲】

【請求項1】 白金、あるいは白金合金とこれを担持するカーボンとからなる触媒と、弗素樹脂との混合物からなるリン酸型燃料電池用電極触媒層の製造方法において、カーボンと弗素樹脂との混合物を支持材上に均一に塗布し、加熱処理して層を形成した後、カーボンのみを除去することにより生成された微細な弗素樹脂のネットワークが形成された弗素樹脂シートに触媒を含浸することを特徴とするリン酸型燃料電池用電極触媒層の製造方法。

【請求項2】 請求項1記載のリン酸型燃料電池用電極触媒層の製造方法において、カーボンと弗素樹脂との混合物を支持材上に均一に塗布し、加熱処理して層を形成した後、この層に電位を印加してカーボンを電解することにより除去することを経ることを特徴とするリン酸型燃料電池用電極触媒層の製造方法。

【請求項3】 請求項2記載のリン酸型燃料電池用電極触媒層の製造方法において、支持材として金、または白金を使用することを特徴とするリン酸型燃料電池用電極触媒層の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、リン酸型燃料電池用電極触媒層の製造方法に係り、特に、触媒層中の白金、あるいは白金合金の利用可能な表面積の減少を防止したリン酸型燃料電池用電極触媒層の製造方法に関するものである。

【0002】

【従来の技術】 従来から、燃料の有している化学エネルギーを直接電気エネルギーに変換する装置として、リン酸型燃料電池が知られている。このリン酸型燃料電池は、通常、リン酸電解質を挟んで一対の電極を配置すると共に、一方の電極に水素等の燃料ガスを供給し、他方の電極に酸素等の酸化剤ガスを供給することにより起こる電気化学反応を利用して、両電極間から電気エネルギーを取り出すようにしたもので、燃料ガス及び酸化剤ガスが供給されている限り、高い効率で電気エネルギーを取り出すことができるものである。

【0003】 通常、この種のリン酸型燃料電池の電極は、電気化学反応を促進するための触媒層と、この触媒層を支持する炭素板とから構成されている。触媒層は白金、あるいは白金合金と、これを担持するカーボンとからなる触媒と、弗素樹脂とによって構成されており、通常次のようにして製造される。

【0004】 すなわち、図4に示すように、まず、触媒1と弗素樹脂2とを混合する。次に、この混合物を炭素板3上に均一に塗布し、ローラにより圧着した後、この圧着体を炉内で所定の温度・時間において熱処理を行うことにより、最終的に触媒層4が形成される。次に、弗素樹脂2を熱処理によって溶解させることにより、触媒

層4内部に微細な弗素樹脂2のネットワークが形成された電極が製造される。このようにして製作された電極は、触媒層4内部の結着性を高めると共に、弗素樹脂2の撥水性によって触媒層4内にリン酸電解質に含浸されない空間を確保し、燃料／酸化剤ガスの流路として活用されている。また、弗素樹脂2の混合量を変えると、触媒層4内のリン酸電解質の含浸量を調節することができる。

【0005】 一般に、燃料電池の運転条件下において、触媒層の撥水性は弗素樹脂の劣化やカーボンの酸化などによって徐々に失われていく。このため、燃料電池の運転に伴い、燃料／酸化剤ガスの流路である気孔がリン酸電解質によって閉塞されてくると、燃料／酸化剤ガスの拡散性が低下し、電池特性も低下することになる。このような燃料電池の経時的な電池特性の低下を抑制するためには弗素樹脂の混合量のある程度増加し、触媒層の撥水性を高める必要がある。

【0006】

【発明が解決しようとする課題】 しかし、触媒層の撥水性を高めるために触媒層の弗素樹脂混合量を増加すると、熱処理によって弗素樹脂を溶解する際に、実際に電気化学反応が行われる白金、あるいは白金合金の表面が、溶解した弗素樹脂によって被覆されてしまい利用可能な表面積が減少するという問題が生じる。

【0007】 ここで、触媒にカーボン担持の白金を使用して、弗素樹脂混合量と実際に電気化学反応に利用されている白金表面積の割合との関係を半電池試験によって調査した例を図3に示す。

【0008】 同図において、弗素樹脂の混合量が35wt%の場合、担持した白金表面積の約93%が電気化学反応に使用されているが、弗素樹脂混合量が増加するに従って利用可能な白金表面積は減少し、混合量50wt%になると、75%程度に減少する。利用可能な白金表面積が減少することは電池特性が低下していることを意味する。

【0009】 触媒層の弗素樹脂混合量を増加すると触媒層にリン酸電解質が含浸する速度が遅くなり、電池寿命は長くなるものの、その反面、電気化学反応に寄与する白金、あるいは白金合金の表面積が減少し、電池特性が低下してしまう。

【0010】 本発明は上記事情に鑑みてなされたもので、その目的は、触媒層の撥水性を損うことなく、弗素樹脂の被覆による利用可能な白金、あるいは白金合金の表面積の減少を防止して電池特性の向上を図ったリン酸型燃料電池用電極触媒層の製造方法を提供することにある。

【0011】

【課題を解決するための手段】 上記目的を達成するために、本発明の請求項1は、白金、あるいは白金合金とこれを担持するカーボンとからなる触媒と、弗素樹脂との

混合物からなるリン酸型燃料電池用電極触媒層の製造方法において、カーボンと弗素樹脂との混合物を支持材上に均一に塗布し、加熱処理して層を形成した後、カーボンのみを除去することにより生成された微細な弗素樹脂のネットワークが形成された弗素樹脂シートに触媒を含浸することを特徴とする。

【0012】本発明の請求項2は、請求項1記載のリン酸型燃料電池用電極触媒層の製造方法において、カーボンと弗素樹脂との混合物を支持材上に均一に塗布し、加熱処理して層を形成した後、この層に電位を印加してカーボンを電解することにより除去することを特徴とする。本発明の請求項3は、請求項2記載のリン酸型燃料電池用電極触媒層の製造方法において、支持材として金、または白金を使用することを特徴とする。

【0013】

【発明の実施の形態】以下、本発明の実施の形態を図を参照して説明する。図1は、本発明の一実施例であるリン酸型燃料電池用電極触媒層の製造方法を示す概要図である。

【0014】同図において、触媒1はカーボンに白金を20wt%の割合で担持したものを、弗素樹脂2はTFE（テトラフルオロエチレン）粉末を、支持材6は金メッシュをそれぞれ使用した。

【0015】まず、弗素樹脂2とカーボン5を10:8の割合とし、分散剤を含んだ溶剤中で攪拌・混合し、ペースト状の混合物を得た。このペースト状混合物を10×10cm²の支持材6にスクリーンプリンタで均一に塗布した。これを340℃の窒素雰囲気中に保たれた炉内で約10分間加熱処理を行い支持材6に層7を形成した。これにより層7中には微細な弗素樹脂のネットワークが形成される。

【0016】次に、この層7+支持材6を1M硫酸中に浸漬し、1.2Vの電位をかけ、層7中のカーボン5のみを電解腐食によって取り除き、微細な弗素樹脂のネットワークで形成された弗素樹脂シート8を得る。そして、炭素板3上に弗素樹脂シート8をローラにより圧着し、炭素板3側を減圧しながら触媒1を弗素樹脂シート8側から吸引含浸し、触媒層4を炭素板3上に形成する。この際、触媒層4には熱処理を行っていない。また、この時の触媒1と弗素樹脂シート8の重量比は1:1となるようにしている。すなわち、弗素樹脂混合量は50wt%となっている。

【0017】このようにして作製した触媒層4中の白金表面の利用率为半電池試験にて測定した結果、白金表面の利用率は95%以上であった。上述したように、既に熱処理している微細な弗素樹脂ネットワークの形成と触媒1の含浸を別の工程で行うことによって、熱処理によって溶解した弗素樹脂2による触媒、すなわち白金表面

への被覆が発生せず、白金表面利用率の低減を防止することができた。

【0018】さらに、この触媒層4を設けた電極を用いた電池の運転履歴と、従来の方法による触媒層を持つ電極を用いた電池の運転履歴とを図2に示した。図2において、従来法による触媒層において、弗素樹脂混合量を40wt%の場合（特性曲線9）から50wt%（特性曲線10）に増すと、電池の寿命は伸びるものの発電初期の電池電圧は低下している。これに対して本発明による触媒層（特性曲線11）の場合、弗素樹脂混合量を50wt%としているにもかかわらず白金表面の利用率が従来例の40wt%の場合（特性曲線9）と比較しても高いため発電初期から電圧が高く、かつ電池寿命も従来例の50wt%の場合（特性曲線10）より長くなっている。

【0019】

【発明の効果】以上説明したように、本発明の請求項1のリン酸型燃料電池用電極触媒層の製造方法によれば、弗素樹脂の溶解と、触媒との混合が別々の工程で行われるため、溶解した弗素樹脂による白金、あるいは白金合金表面への被覆が発生せず、触媒層中の白金、あるいは白金合金の利用可能な表面積の減少を防止することができる。

【0020】本発明の請求項2によれば、物理的、機械的にカーボンを除去するのではなく、電気化学的にカーボンを除去することによって、微細な弗素樹脂ネットに捕われているカーボンを完全に除去することが可能となる。

【0021】本発明の請求項3によれば、カーボンと弗素樹脂との混合物の層を、導電性があり、化学的に安定な金、あるいは白金のメッシュ上に形成することによって、そのまま電解処理を行うことが可能となるので、より容易に作業することができる。

【図面の簡単な説明】

【図1】本発明の一実施例のリン酸型燃料電池用電極触媒層の製造方法を示す概要図。

【図2】従来の触媒層を持つ電極と本発明による触媒層を持つ電極を用いた燃料電池の経時特性を示した図。

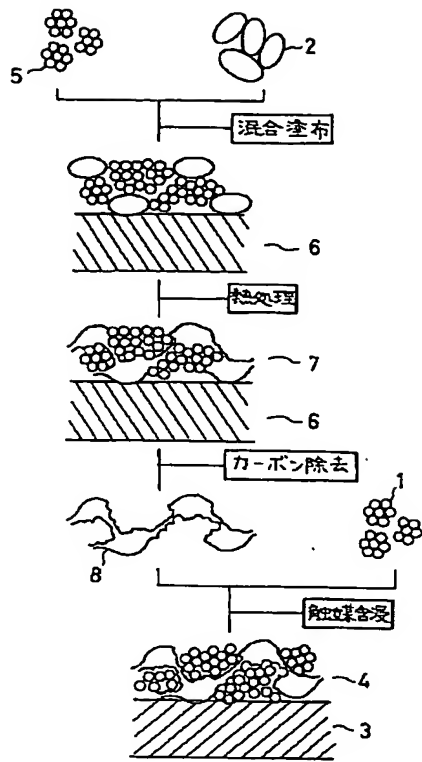
【図3】従来の製造方法によるリン酸型燃料電池用電極触媒層の弗素樹脂混合量と触媒層の白金表面の利用率为示す図。

【図4】従来のリン酸型燃料電池用電極触媒層の製造方法を示す概要図。

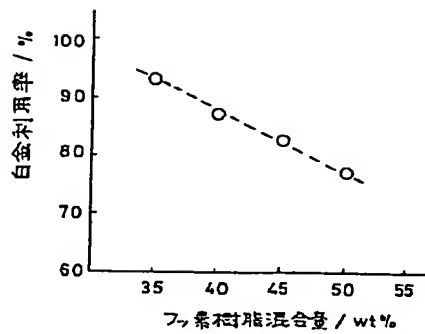
【符号の説明】

1…触媒、2…弗素樹脂、3…炭素板、4…触媒層、5…カーボン、6…支持材、7…層、8…弗素樹脂シート。

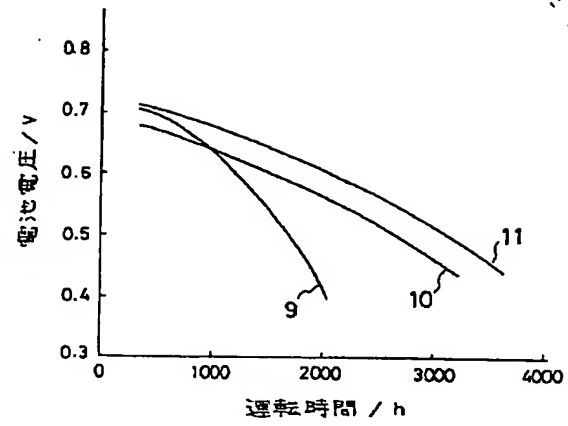
【図1】



【図3】



【図2】



【図4】

